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# EXPOSURE OF APPLE THINNERS TO PARATHION RESIDUES

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In studies of potential exposure of a volunteer working under controlled conditions during apple hand-thinning operations at 1, 24, 48, 72, 96, 168, and 240 hr after application of conventional 0.03% parathion spray, both dermal and respiratory exposure values were greater where water-wettable powder formulations were used than where emulsifiables were used. Residue levels of parathion on leaves from the two types of applications were about the same. Only trace amounts of paraoxon could be detected at one and seven days after application. Highest exposure values (14.2 mg/hr dermally and 0.15 mg/hr respiratorily) were obtained within 24 hr of application. Exposure was considerably less after residues were 72 hr old. Greatest exposure was on the forearms and hands. Urinary *p*-nitrophenol excretion indicated slightly more absorption following exposure in water-wettable powder experimental plots. Potential exposure values indicate that absorption could reach hazardous levels after one or two hr of work, even at the 96-hr residue period, if all the pesticide were absorbed. Considering that only a small fraction of the total amount would be absorbed, it is calculated that at 72-hr residue period poisoning should not occur. There was no significant change in blood cholinesterase activity of the volunteer worker. Variation in spray deposit within an orchard due to poor tank mixing did not appear to be great enough to be considered an important factor affecting exposure.

Quinby and Lemmon (1958) reported outbreaks of poisoning in apple thinners and orchard irrigators in Central Washington resulting from exposure to the organophosphorus pesticide, parathion (*O,O*-diethyl *O*-*p*-nitrophenyl phosphorothioate), as early as 1952. By that time the use of this pesticide in orchards was becoming widespread. They reported five outbreaks from 1952 through June 1957. Unpublished case records on file at this laboratory indicate that more residue poisonings were brought to our attention in Washington State during 1958 than in any other year. During that period the use of parathion in orchards was nearing its peak. Since that time the number of cases of poisoning of thinners has dropped to a very low level. This could be partly due to changes in spray practices, including reduced use of parathion during the thinning period, and the increased utilization of chemical thinning practices. However, crop reentry period recommendations of at least 48 hr (Washington State College 1958), and preferably more than three days (Washington State University 1971), following parathion application to apples in Washington State may also be a factor.

An unanswered question in relation to parathion poisoning of apple thinners is why some workers become ill while other workers are apparently unaffected under what ap-

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pears to be the same conditions. This suggests that there may be factors that come into play in some situations that may cause illness in workers in a particular orchard and at a particular time under specific conditions.

The purpose of this paper is to report research to determine the potential dermal and respiratory exposure during hand-thinning activities in parathion sprayed apple orchards and to obtain information concerning certain factors that may be involved in increased health hazard to such workers.

## Materials and methods

Our attempts to obtain meaningful comparative potential dermal and respiratory exposure values for workers hand-thinning apples under commercial orchard work conditions has been less than adequate, primarily because of lack of proper control of worker activities. Thus, in order to obtain more valid results in comparing exposure where different parathion formulations were used or to properly carry out tests during thinning activities at different periods following pesticide application, one of the authors (HW) worked as a volunteer thinner so that the experiments would be under controlled conditions and the work movements and measurements could be kept as nearly the same as possible for each thinning test period. A limited number of samples to determine potential dermal and respiratory exposure were also obtained using regular thinning crews working in commercial orchards.

Three series of controlled tests were carried out by the volunteer worker. The first involved measurement of potential dermal and respiratory exposure during one-hr work periods at 1, 24, 48, and 96 hr after application in a commercial orchard where spray containing approximately 0.03% parathion, 0.12% DDT (1,1,1-trichloro-2,2-*bis*(*p*-chlorophenyl)ethane), and 0.04% dicofol (4,4'-dichloro-α-(trichloromethyl)benzhydrol) was applied. The second series of tests was carried out through the 96-hr period following application in an experimental orchard plot where the dosage was carefully controlled and foliage was sampled to determine the level of parathion residue each day. This series was also designed to include a comparison of exposure where water-wettable powder formulations of the pesticides were used in the spray, with exposure where liquid emulsifiable concentrate formulations were used.

In order to simulate the usual field applications, spray solutions containing 0.03% parathion, 0.12% DDT, and 0.04% dicofol, utilizing water-wettable powder formulations, were used in one-half of the experimental orchard, and spray solutions of the same concentrations using liquid emulsifiable concentrate formulatons of parathion and dicofol were used in the other half. The emulsifiable concentrate formulation of DDT could not be used due to potential phytotoxic effects on apples. Spray was applied at the rate of approximately 5,610 L/ha (600 gal/A) by use of an air-blast spray machine. Applications were timed so that fruit thinning could be conducted in each plot for a period of one hr with the start of each thinning test at approximately one hr following spray application. The same order of thinning was followed each day through the 96-hr residue period. Thinning in the

two orchard plots each day was then accomplished by the volunteer worker under approximately the same conditions of temperature, wind, etc.

The third series of tests was similar to the second, with the exception that it was carried out through the 240-hr period following application and included the collection of total urine passage from the volunteer worker in order to obtain some information concerning the amount of parathion absorbed through determination of *p*-nitrophenol excreted.

Although blood cholinesterase levels were checked on the volunteer thinner, results were not intended to reflect conventional exposure because thinning tests were conducted for only two hr per day for each series as compared with a 10-hr daily exposure for most workers.

Estimation of the amounts of exposure that the worker would potentially incur through impingement of pesticide onto exposed body areas and through the respiratory route followed the exposure pad and hand rinse techniques and procedures described in detail by Durham and Wolfe (1962). Potential dermal contamination was measured primarily by attaching layered gauze pads to various parts of the body or clothing of workers and allowing them to become contaminated during a timed interval of work. However, dermal contamination of the hand areas was, in most cases, measured by use of the bag rinse technique with 95% ethyl alcohol as the solvent. Respiratory exposure was estimated from the contamination of filter pads held in special single-unit respirators.

In a study of factors affecting exposure of apple thinners, spray concentration and foliage residue tests were carried out in an attempt to define any variation in pesticide coverage within an orchard. The tests were designed to explore the possibility that certain spray machines might have inefficient agitator equipment and, because of higher spray concentration either at the beginning or end of a tank, could result in much higher than normal residues on fruit, foliage, and twigs on some trees. The first step in the procedure was to establish the exact spraying time for each spray machine checked. Samples of dilute spray were then collected as it was emitted from the nozzles one min after spraying started, when the tank was approximately half empty, and again during the last minutes of spraying before the tank became empty. These samples were analyzed to determine spray concentration. When a sample of spray was collected, the tree being sprayed at the time was flagged and leaf samples were collected for residue analysis after the tree had been sprayed from the opposite side during normal progression of the spray machine through the orchard.

At the time of the experiment the need for determining dislodgeable residues in addition to total leaf residues was not as apparent as it is today; therefore, only total leaf extraction was employed using ethanol as a solvent.

Analysis for parathion and paraoxon was by gas liquid chromatography using electron capture or flame photometric detectors. Analysis for the parathion urinary metabolite, *p*-nitrophenol, was by the method of Elliott *et al.* (1960). Blood cholinesterase determinations were by the method of Michel (1949).

## Results and discussion

Results of the first series of controlled exposure tests are shown in Table I. The highest potential dermal exposure value obtained (14.2 mg/hr of exposure at the 24 hr residue period) is only slightly less than the 19.4 mg/hr calculated average dermal exposure for spraymen applying parathion with air-blast spray machines in apple orchards, published earlier by this laboratory (Wolfe *et al.* 1966). The highest potential exposure *via* the respiratory route (0.15 mg/hr of exposure at the one-hr residue period), however, is approximately eight times greater than that calculated for these spraymen. Even at the 96-hr period the potential respiratory exposure of 0.03 mg/hr obtained for thinning is greater than the 0.02 mg/hr calculated as average respiratory exposure for the sprayman using an air-blast spray machine applying parathion at a 0.03% spray.

Results of the second and third series of controlled exposure studies are shown in Tables II and III. In both studies potential exposure was found to be two to three times greater when working in water-wettable powder plots than when in the liquid emulsifiable plots. Some of this may have been due to the slightly higher initial residue levels on the foliage in the water-wettable powder plots; however, we feel that much of the difference was due to the ease with which the dried residue from the water-wettable powder formulations dislodged from the foliage during contact or agitation by the worker. During thinning where water-wettable powder was used, "dusty" conditions were easily observed under proper light conditions. The worker felt that dust was collecting in his mouth, nose and throat, occasionally causing him to sneeze. This was not the case where emulsifiable concentrate formulations were used. In Tables II and III it is shown that potential exposure when working in 24-hr residues in the water-wettable powder plots was as great as or slightly greater than when working in the same plots when the residues were only one hr old. The reason may be that the spray deposit on the foliage, which initially appeared to be slightly sticky, did not become thoroughly dry until about 24 hr have elapsed. By that time the wettable powder and other particulate material may be more easily dislodged during fruit thinning activities. The volunteer worker noted more particulate material in the air during work activity at the 24-hr period than at the one-hr period following application.

**Table I.** *Potential dermal and respiratory exposure of a volunteer apple thinner to parathion in an orchard sprayed with 0.03% parathion, 0.04% dicofol and 0.12% DDT solutions prepared from water-wettable powder formulations—Series 1*

| Reentry time after spraying (hr) | Exposure (mg/hr)[a] | |
|---|---|---|
| | Dermal | Respiratory |
| 1 | 11.3 | 0.15 |
| 24 | 14.2 | 0.13 |
| 48 | 8.4 | 0.06 |
| 72 | 8.1 | 0.05 |
| 96 | 4.8 | 0.03 |

[a]Calculated on the basis of the worker wearing a shortsleeved, open-necked shirt, no gloves or hat, with his clothing giving the only protection of the areas covered. One-hr exposure periods.

**Table II.** *Potential dermal and respiratory exposure of a volunteer apple thinner to parathion in orchards sprayed with 0.03% parathion, 0.04% dicofol and 0.12% DDT solutions prepared from emulsifiable concentrate or water-wettable powder formulations—Series 2*

| Reentry time after spraying (hr) | Emulsifiable concentrate plot[a] | | | Water-wettable powder plot | | |
|---|---|---|---|---|---|---|
| | Exposure (mg/hr)[b] | | Residue on leaves[c] ($\mu g/cm^2$) | Exposure (mg/hr)[b] | | Residue on leaves[c] ($\mu g/cm^2$) |
| | Dermal | Respiratory | | Dermal | Respiratory | |
| 1 | 6.0 | 0.035 | 4.0 | 11.3 | 0.150 | 4.7 |
| 24 | 4.4 | 0.020 | 2.4 | 12.4 | 0.146 | 2.9 |
| 48 | 2.2 | 0.027 | 1.7 | 8.9 | 0.078 | 2.3 |
| 72 | 1.8 | 0.023 | 0.8 | 5.7 | 0.029 | 1.2 |
| 96 | 1.0 | 0.011 | 0.6 | 2.4 | 0.023 | 0.9 |

[a]DDT not used in this plot.
[b]Calculated on the basis of the worker wearing a short-sleeved, open-necked shirt, no gloves or hat, with his clothing giving the only protection of the areas covered. One-hr exposure periods.
[c]Mean values for three samples each period.

**Table III.** *Potential dermal and respiratory exposure and urinary p-nitorophenol levels of a volunteer apple thinner resulting from work activities in orchards sprayed with 0.03% parathion, 0.04% dicofol and 0.12% DDT solutions prepared from emulsifiable concentrate or water-wettable powder formulations—Series 3*

| Reentry time after spraying (hr) | Emulsifiable concentrate plot[a] | | | | Water-wettable powder plot | | | |
|---|---|---|---|---|---|---|---|---|
| | Exposure (mg/hr)[b] | | *p*-Nitrophenol excretion[c] (mg/24-hr period) | Residue on leaves[d] ($\mu g/cm^2$) | Exposure (mg/hr)[b] | | *p*-Nitrophenol excretion[c] (mg/24-hr period) | Residue on leaves[d] ($\mu g/cm^2$) |
| | Dermal | Respiratory | | | Dermal | Respiratory | | |
| 1 | 4.1 | 0.031 | 0.033 | 2.8 | 7.6 | 0.131 | – | 3.9 |
| 24 | 3.7 | 0.012 | – | 1.8 | 9.9 | 0.110 | 0.057 | 2.1 |
| 48 | 1.7 | 0.017 | 0.032 | 1.4 | 7.0 | 0.062 | – | 1.7 |
| 72 | 1.6 | 0.016 | – | 0.9 | 5.3 | 0.042 | 0.031 | 1.1 |
| 96 | 1.1 | 0.009 | 0.013 | 0.3 | 3.7 | 0.029 | – | 0.7 |
| 168 | 0.5 | 0.007 | – | 0.1 | 1.2 | 0.013 | 0.016 | 0.2 |
| 240 | 0.5 | 0.006 | – | 0.1 | 0.8 | 0.008 | – | 0.2 |

[a]DDT not used in this plot.
[b]Calculated on the basis of the worker wearing a short-sleeved, open-necked shirt, no gloves or hat, with his clothing giving the only protection of the areas covered. One-hr exposure periods.
[c]The values given represent *p*-nitrophenol excretion (expressed as parathion equivalent) during the 24-hr period during and following thinning exposure at the indicated time after spraying.
[d]Mean values for three samples each period.

Data in the tables show that residues of parathion on leaves from the two types of application were approximately the same at each test period with a loss of one-half the original residue within approximately 48 hr after application.

In a limited study to determine the amount of paraoxon in foliage residues following parathion application to apples during a one-week period in June, only trace amounts could be detected. At one day following application of a 0.03% parathion spray where a water-wettable powder formulation was used, the amount of paraoxon detected was 48 ng/cm$^2$ of leaf surface. Seven days after application only 8 ng/cm$^2$ could be detected. These values can be compared with 1320 and 106 ng/cm$^2$, respectively, found at these intervals, for parathion.

In order to compare the relative potential exposure for different unprotected body parts, additional tests were carried out involving regular workers in orchards as well as the controlled volunteer. This work involved tests in 56 different thinning exposure situations over a three-year period. The data are in Table IV. The forearms and hands obviously are the unprotected body areas subjected to the greatest potential exposure during apple thinning operations, with the face area subject to the next highest exposure. It is interesting to note that the collection of pesticide on the forearms is almost twice as much, per hr of work, as on the hands which come in firm contact with residues on the small apples.

Based on the assumption that a 60 kg adult can absorb three mg of parathion daily without cholinesterase depletion and 7.2 mg daily for a period of six weeks without illness, and with minimal cholinesterase depletion (Edson 1957, 1964), the potential exposure values shown in Tables I, II, and III indicate that absorption could reach hazardous levels within one or two hr of work activity, even at the 96-hr period, if all the measurable pesticide available for dermal and respiratory exposure was completely absorbed. By multiplying the values by ten to arrive at potential exposure values for a 10-hr work day, it is evident that the amount of absorption that actually occurs under field conditions is only a small fraction of the amount available on the skin; otherwise, apple-thinner's poisoning would occur more frequently. Earlier studies at this laboratory, using excretion of *p*-nitrophenol as an indicator of parathion absorption, indicated that dermal absorption was only 0.1 to 2.8% of

**Table IV.** *Comparison of potential dermal exposure values for unprotected body parts to parathion per hour of hand-thinning apples for 56 work situations studied (regular workers as well as controlled volunteer) regardless of reentry period following spray application*

| Body part | Total calculated exposure (mg/body part/hr) | |
|---|---|---|
| | Range | Mean |
| Face | 0.10 - 3.6 | 1.0 |
| Front of neck, "V" of chest | 0.02 - 0.5 | 0.1 |
| Back of neck | 0.01 - 0.4 | 0.1 |
| Forearms | 0.30 - 8.2 | 2.5 |
| Hands | 0.08 - 4.0 | 1.5 |

the potential dermal exposure (Durham and Wolfe 1963). If these absorption values are correct, then, when thinning apples with residues that were at least 72 hr old, the amount of absorption during a 10-hr day would not exceed Edson's three mg per day value which he found did not result in measurable cholinesterase reduction. This tends to support a recommendation that a 72-hr reentry waiting period for workers in apple orchards sprayed with parathion is safe and would also provide some explanation as to why most of the apple thinner's poisonings have occurred in those persons who worked in orchards within 48 hr of application.

*p*-Nitrophenol excretion values for the volunteer worker as noted in Table III reflect absorption resulting from only two hr of work each day, alternating between emulsifiable and water-wettable powder plots. Also, the worker wore a respirator part of the time. Therefore, calculations from these excretion values may not accurately reflect absorption during a normal 10-hr work day. The values do indicate slightly greater absorption where exposure was greater in the water-wettable plots. There is also some indication that absorption of parathion was considerably less when working in residues 96 hr or more in age than when working in residues 1 to 24 hr old.

Blood samples taken from the volunteer worker prior to and following the exposure series were analyzed for cholinesterase activity. No significant change was noted.

Results of the study of spray concentrations in spray machine tanks at different periods during spraying operations are in Table V. The range and mean values for 20 spray machines using water-wettable powder and 15 using liquid emulsifiable concentrate are shown. Where water-wettable powder was used there was slightly more variation in spray concentrations than where the liquid emulsifiable concentrate was used. The highest value (0.062%) for concentration found during the first min of spraying from the tank where water-wettable powder was used was over twice the 0.03% calculated concentration assuming uniform mixing throughout the tank. However, mean values were near the calculated concentration. The higher concentration emitted during the first min may be due to the tendency of the material to settle toward the bottom of the tank where it is relatively near the pump inlet when bagsful of pesticide are dumped into the tank during loading operations. In normal practice the operator rarely adds pesticide to the tank before it is at least one-half full and in most cases two-thirds to three-fourths full. The mixing or agitator mechanism usually varies with the engine speed which is normally held at idle during loading. This may result in inefficient mixing until the engine speeds up at or near the start of spraying. Considering how rapidly a tank is filled and how quickly a spray machine is usually in operation after filling is completed, it is surprising that the pesticide is mixed as well as it is by the time the first few trees are sprayed

Results of analyses of residues of parathion on apple foliage receiving spray from different levels of the tanks are in Table VI. There was slightly more variation in deposit where the water-wettable powder formulation was used than where the emulsifiable concentrate formulation was used. This coincides with the slight variation in concentration of spray in the tanks. The mean values, however, are the same. Under normal spray opera-

**Table V.** *Concentration of parathion spray emitted from different portions of tank during spray operation*

| Pesticide formulation used | No. replicates | Concentration of spray from different portions of tank (%)[a] | | | | | |
|---|---|---|---|---|---|---|---|
| | | First | | Middle | | Last | |
| | | Range | Mean | Range | Mean | Range | Mean |
| Water-wettable powder | 20 | 0.017 - 0.062 | 0.032 | 0.022 - 0.040 | 0.030 | 0.017 - 0.035 | 0.026 |
| Liquid emulsifiable concentrate | 15 | 0.010 - 0.045 | 0.028 | 0.019 - 0.035 | 0.029 | 0.011 - 0.042 | 0.028 |

[a]Calculated concentration based on uniform mixing was 0.03%.

**Table VI.** *Deposit of parathion on apple foliage sprayed from different portions of tank*[a]

| Pesticide formulation | No. replicates | μg/cm² of leaf surface | | | | | |
|---|---|---|---|---|---|---|---|
| | | First | | Middle | | Last | |
| | | Range | Mean | Range | Mean | Range | Mean |
| Water-wettable powder | 20 | 1.9-5.2 | 3.8 | 1.8-6.2 | 3.6 | 2.0-7.8 | 4.3 |
| Liquid emulsifiable concentrate | 15 | 3.0-4.9 | 4.1 | 3.2-5.0 | 4.2 | 2.0-5.0 | 3.8 |

[a]After trees sprayed from both sides.

tions where trees are sprayed from both sides as the machine progresses up and down orchard tree rows the same extremes in spray concentrations would rarely coincide. When they do not coincide the effect should be to even out the deposit on the foliage throughout an orchard because the spray tends to carry through the trees from one side to the other. In cases where both sides of trees are sprayed with either high or low concentrations, higher or lower residues should result.

It is of interest to note that the highest residue value obtained (7.8 μg/cm² of leaf) is about twice as high as the mean residue value. It is doubtful that workers thinning fruit would be exposed to this higher level for any great period of time because our observations indicate that not more than three or four trees would receive the higher treatment from both sides.

Results of the present studies do not pinpoint any unusual factors that might appreciably increase the health hazard to workers hand-thinning apples following application of parathion other than the finding that exposure is greater where water-wettable powder formulations are used. In studying the potential dermal and respiratory exposure values obtained in the controlled studies, one could arrive at the conclusion that the potential exposure to parathion was great enough to be considered hazardous in certain instances, should all of the material be absorbed by the body, without considering the possibility of occasional higher than normal levels of more toxic metabolites. Obviously, only a low percentage of parathion is absorbed; otherwise poisoning cases would occur more frequently. The data indicate that potential exposure is reduced considerably after 72 hr have elapsed following application. This appears to agree with field experience in the Pacific Northwest where it is felt that a 72-hr delay following parathion application is a safe reentry period for apple thinners.

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